TRANSPORT PHENOMENA

by J. D. Hellums

The term "transport" is often applied to the study of phenomena governing the rates of flow of mass, energy, and momentum. Hence, the term applies to almost all processes of engineering interest. Let us suppose that our objective is to study some process in detail and to develop a mathematical model by which we can predict, and thereby improve, the design or operation of the process. If we fall somewhat short of perfection in this objective, which will almost certainly be the case with biological processes, we will find that even a partial analysis or highly simplified model often yields important information. In such a study we may think of certain properties of the system as being dependent variables whereas the independent variables are position in space and time. For example, we might wish to determine concentrations of the various chemical and/or bacterial species, temperature, and pressure, at all positions and times in the process.

The principal restrictions which, in principle, determine the dependent variables are listed below:

1) The transport equations governing the rates of change of momentum, energy, and mass.

2) Chemical kinetic expressions. The usual point of view in chemical kinetics is that the rate of appearance (or disappearance) of a particular species[1] per unit of volume at a particular point is dependent only on the intensive properties of the system, at the position and time of interest. Such a point of view is, of course, applicable only when a species is well identified. That is to say, it would be erroneous to regard the total mass of some organism as a species, if subtle changes in the organism change its kinetic response to its environment. In any case, the rate of appearance of a species due to chemical reactions will be considered separately from the transport equations. In a subsequent paper the kinetic relationships will be discussed in more detail. In this paper we will assume that the simplest sort of kinetic relationships hold since we are primarily interested in the transport phenomena.

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3) Thermodynamic and stoichiometric relationships. The laws of thermodynamics and the stoichiometric restrictions are included in the transport and kinetic expressions., However, they warrant separate consideration since they can be developed and employed independently and are applicable in cases where the transport equations are not easily solved or even formulated.

4) Equations of state such as the gas laws, and other equations governing the dependence of physical properties on pressure, temperature, and composition.

All of these restrictions are important in the study of various physical processes. It is the purpose of this paper to focus attention on only one of these important expressions: the expressions governing transport of mass. An introductory discussion of the basic transport relationships and idealizations will be given together with several example applications in fields allied to water technology. The presentation is directed to workers in water technology who are in need of review or who, for any reason, are not well versed in mathematical methods of analyzing transport problems. Several texts are available on the topic.[2]

The Mass Flux in One Dimension

The flux of a quantity is defined to be the rate of flow per unit cross sectional area with the cross sectional area understood to be normal to the direction of flow. Hence, the flux is a vector having the direction of the flow of the quantity under consideration.

The flow of energy, mass, and momentum is customarily divided into two parts: the convective flux (due to ordinary flow of fluid), and the flux due to molecular motion, or diffusion. The total convective mass flux is given by $u\rho$, the product of the velocity vector and density, with dimensions mass per unit time per unit area. Similarly, the convective mass flux[3] of species "A" is simply given by $W_A u\rho$ where W_A is the weight fraction of species "A." In molar units the convective flux of species "A" is given by $C_A u$, where C_A is concentration in moles per unit volume, and the flux is in moles per unit time per unit area.

The convective flux depends on bulk motion of the fluid. Superimposed on the convective flux is the flux due to molecular motion or diffusion.

The flux of species "A" in the x direction due to diffusion or molecular motion under conditions of approximately constant total molar density is given by Fick's law:

$$-D_A \frac{dC_A}{dx} \qquad (1)$$

where it is assumed that the concentration of species "A" is dependent only on x.

Hence, the total flux of "A" in the x direction, N_{Ax}, is the sum of the convective and diffusion fluxes, which for dilute solutions is approximately given by

$$N_{Ax} = u_x C_A - D_A \frac{dC_A}{dx} \tag{2}$$

where u_x denotes the x component of the velocity vector. If C_A varies other than in the x direction $\frac{dC_A}{dx}$ is replaced by $\frac{\partial C_A}{\partial x}$.

Rate Limitation by Diffusion

Film Theory

The film theory approach to diffusion problems is highly oversimplified in concept, yet has been found useful for many years in a qualitative, and in some cases, a quantitative way. Consider a simple example wherein species "A" diffuses through a stagnant "film" to the interface of a bacterium phase. Neglecting convection currents, we find the derivative $\frac{dC_A}{dx}$ is simply the slope of the straight line concentration profile

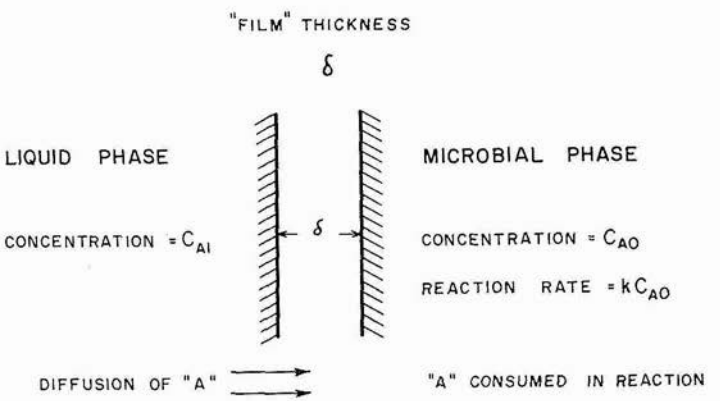

FIGURE 1 - FILM MODEL FOR DIFFUSION

$\frac{dC_A}{dx} = \frac{C_{AI} - C_{AO}}{\delta}$ (See Figure 1.) Hence the total flow rate of species "A" into the microbial phase is given by

$$R = D_A \frac{C_{A1} - C_{A0}}{} S \tag{3}$$

in moles per unit time, where S is the total interfacial area. Assuming the microbial phase may be represented by a first order homogeneous reaction yields an expression for the rate of disappearance of A in the reaction.

$$R = \frac{D_A (C_{A1} - C_{A0}) S}{\delta} = kC_{A0} V \tag{4}$$

where k is the reaction rate constant and V is the total microbial phase volume. Solving for C_{A0} and rearranging, yields:

$$R = \left[\frac{kV}{1 + \frac{kV\delta}{D_A s}}\right] C_{A1} \quad ; \quad C_{A0} = \frac{C_{A1}}{1 + \frac{kV\delta}{D_A s}} \tag{5}$$

The coefficient in square brackets may be regarded as an "apparent first order reaction rate constant" since it is based on the measurable concentration C_{A1} in the bulk liquid and the overall rate of disappearance of "A." However, it is important to note that the coefficient need not be related to reaction rates at all. In the case of low diffusion coefficients, as is invariably the case in liquids, it often occurs that $\frac{kV\delta}{D_A S} >> 1$ in which case $R = \frac{D_A S C_{A1}}{\delta}$ and $C_{A0} << C_{A1}$. In this case the apparent reaction rate constant is determined entirely by the mass transfer problem and has no connection with kinetics whatever. On the other hand, in cases where the parameter $\frac{kV\delta}{D_A S}$ is small, relative to unity, $C_{A0} \approx C_{A1}$, $R \approx kV C_{A1}$ and the apparent reaction rate constant approaches the correct reaction rate constant. This simple example illustrates the importance of taking transport phenomena into account in studying rate processes. Many studies have been made on reaction rates which in reality measured only diffusion rates. Needless to say, if one is primarily interested in studying diffusion, it is preferable to construct a very simple system where the diffusion is studied in as nearly an isolated way as is possible. Conversely, if one is primarily interested in studying reactions, the transport phenomena represents an always-present complication which can, and often does, mask the phenomenon of main interest.

Extension to Spherical Shapes—Rate Limitation in BOD Progression

Of interest is the extension of the film theory example to diffusion to spherical particles or microbes. In this way we can eliminate the ill-

defined film parameter, δ , and solve a problem in which all parameters are easily visualized. Neglecting convection currents again, the flux of species "A" toward the center of the sphere is $D_A \frac{dC_A}{dr}$. Hence, the rate of disappearance of "A" for m identical particles is the flow rate through the area $4\pi r^2$ per particle:

$$R = m\, D_A \frac{dC_A}{dr} \left(4\, \pi r^2\right) \tag{6}$$

Neglecting accumulation or depletion of "A" in the region near the sphere we find R is independent of r. The equation may be directly integrated and rearranged to yield the rate

$$R = 4\pi m\, D_A\, r_0 \left[C_{A1} - C_{A0}\right] = kVC_{A0} \tag{7}$$

where the second of the equations is the assumed first order reaction rate expression. V denotes the total microbial volume and r_0 the radius. C_{A1} is the concentration in the bulk liquid a long distance from the particle. Rearrangement as before yields:

$$R = \left[\frac{k}{1 + \frac{kV}{4\pi m D_A r_0}}\right] VC_{A1} \quad ; \quad C_{A0} = \frac{C_{A1}}{1 + \frac{kV}{4\pi m D_A r_0}} \tag{8}$$

As in the film theory example, the quantity in square brackets may be regarded as an apparent reaction rate constant which is based on the observable concentration, C_{A1}. Consider two limiting cases as before. For a relatively slow reaction ($\frac{kV}{4\,\pi\, m\, D_A\, r_0}$ negligible next to unity) the apparent rate constant approaches k, the "true" rate constant. On the other hand, if the quantity $\frac{kV}{4\,\pi\, m\, D_A\, r_0}$ is large relative to unity, the apparent rate constant approaches $\frac{4\,\pi\, m\, D_A\, r_0}{V}$, a quantity having no connection with reaction rates. The reaction is said to be diffusion controlled in the later case.

Swilley, Bryant and Busch[4] have considered this example in a study on BOD progression by the bottle technique. From the measurements of Busch, et al.,[5] they calculated or estimated the apparent reaction rate constant and each of the other parameters in the rate expression. Their conclusion was that the reaction is diffusion controlled. Hence, studies of this type which report results in terms of reaction rate constants are subject to reinterpretation.

A Model for Microbial Growth with Diffusion

The simple diffusion-reaction model described above can easily be extended to account for the observed behavior of microbial systems. For example, the familiar bacterial growth curve shown in Figure 2

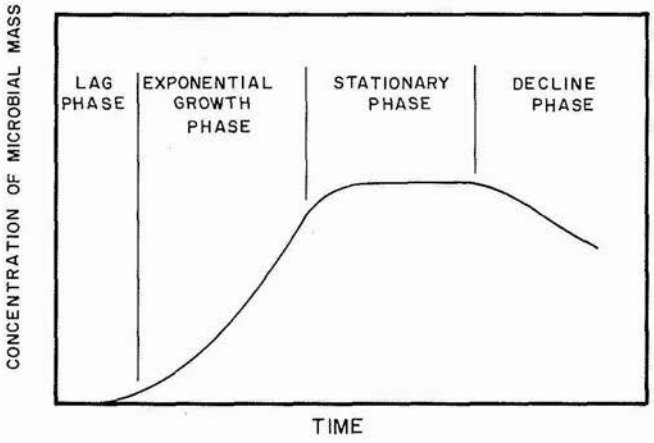

FIGURE 2 - IDEALIZED BACTERIAL GROWTH CURVE

can be reproduced in detail by a relatively simple model consisting of a pair of reactions in which the biomass reacts with substrate to produce both biomass and an inhibitor. The inhibitor in turn is presumed to react with active biomass to produce a biomass incapable of further reaction. See for example the recent work of Ramkrishna, Fredrickson and Tsuchiya.[6] In this volume, Deans discusses more general models.[7] These workers consider kinetic models neglecting the influence of diffusion. It is interesting to show here that the observed behavior of microbial systems can be partially accounted for by a simple diffusion-controlled mechanism. We will confine our attention to integration of two cases involving the simple model already introduced.

Exponential Growth

Suppose that in the growth reaction each mole of species "A" consumed yields $\frac{1}{\alpha}$ units of microbial volume. Then $R = \alpha \frac{dV}{dt}$ and from equation (8) we have

$$R = \alpha \frac{dV}{dt} = \left[\frac{k}{1 + \frac{kV}{4\pi m D_A r_0}} \right] V C_{A1} \tag{9}$$

$$= KVC_{A1} \tag{10}$$

where K denotes the apparent reaction rate constant, the quantity in square brackets in equation (9). If the microbial phase is of fixed configuration (V/m constant and r_0 constant) it is plausible to assume K is constant. Hence, if C_{A1} is constant, we obtain by direct integration the familiar exponential expression

$$V = V_i \, e^{\frac{k}{\alpha} C_{A1} \, t} \tag{11}$$

where V_i is the initial volume of microbial phase.

Diffusional Depletion of Substrate

In a more general case where the amount of "A" is limited, C_A changes with time in accordance with the balance

$$R = \frac{-d}{dt}\left(V_S \, C_A\right) \tag{12}$$

where V_S is the volume of the liquid phase, assumed constant. Simultaneous solution of equations (12) and (9) yields

$$V = V_i \frac{e^{gt}}{1 - \left[\frac{f}{1+f}\right]\left[1 - e^{gt}\right]} \tag{13}$$

where $f = \frac{V_i \, \alpha}{V_s \, C_i}$, C_i is the initial concentration of "A" and

$$g = \frac{k}{\alpha} C_i \left(1 + f\right) \tag{14}$$

Of interest is that equation (13) correctly describes several limiting cases:

1) Small times. In this case the equation reduces to exponential growth, as in equation (11), as would be expected before appreciable amounts of "A" have been depleted. The denominator in the equation approaches unity as t becomes small.

2) Large times. At large times the exponential terms dominate and cancel one another yielding

$$V = V_i \left[\frac{1+f}{f}\right] = V_i + \frac{V_S \, C_i}{\alpha} \tag{15}$$

which is the stationary phase microbial volume. We see the expression asymptotically approaches the stoichiometrically correct stationary phase biomass.

3) Infinitely large V_s. In this case f approaches zero, corresponding to no depletion of substrate. Hence, the exponential growth case results again because the denominator approaches unity. This behavior is also

correct for finite times since we have assumed unlimited substrate.

Note again that equation (13) need not have any connection with kinetics, as indicated in the prior discussion of diffusion controlled reactions. In contrast, the models discussed by Deans,[8] and Ramkrishna, et al.,[9] are entirely kinetic models which neglect the influence of diffusion.

Equations of Change

In the prior examples we have in each case chosen simple enough conditions so that the quantities of interest were dependent on only one variable—either radial position or time. While such examples are useful, they cannot describe adequately processes of major interest wherein three space coordinates as well as time are the independent variables. The more general transport relationships are partial differential equations for the rates of change of momentum, energy, and mass. As an introduction to the subject, we will now consider the development of one of the relationships: the rate of change of mass of species "A" in cartesian coordinates for dilute solution.

A One-Dimensional Balance

Consider a problem involving flow (and changes of any type) in only one direction, the x direction. The material balance on species "A" may be written

$$\begin{matrix}\text{Inflow}\\ \text{rate}\end{matrix} = \begin{matrix}\text{Outflow}\\ \text{rate}\end{matrix} + \begin{matrix}\text{Accumulation}\\ \text{rate}\end{matrix} + \begin{matrix}\text{Disappearance}\\ \text{rate}\end{matrix} \qquad (16)$$

Consider a volume element of Δx units length and S units cross sectional area as indicated in Figure 3. The accumulation rate is the time derivative

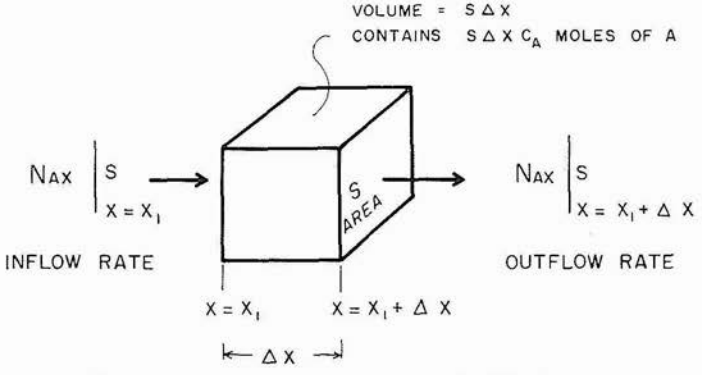

FIGURE 3 - DIFFERENTIAL MATERIAL BALANCE

of the amount "A" in the system. Let V_0 be the rate of disappearance of "A" per unit volume. Note that $S\Delta x$ is the volume of the system. Hence, the complete balance is

$$N_{Ax}\Big|_{x=x_1} S = N_{Ax}\Big|_{x=x_1+\Delta x} S + \frac{\partial}{\partial t}\left[C_A\, S\Delta x\right] + r_A\, S\Delta x \qquad (17)$$

where C_A and r_A are average values in the system. Division by $S\Delta x$ and rearrangement yields

$$\frac{\partial C_A}{\partial t} = \frac{-\left(N_{Ax}|_{x_1+\Delta x} - N_{Ax}|_{x_1}\right)}{\Delta x} - r_A \qquad (18)$$

If we take the limit as Δx vanishes, the average values approach the values at $x = x_1$ and the quotient becomes the derivative at the point $x = x_1$. Since all quantities are at the point $x = x_1$ we can delete the subscript if we wish.

$$\frac{\partial C_A}{\partial t} = \frac{-\partial N_{Ax}}{\partial x} - r_A \qquad (19)$$

Substitution of $N_{Ax} = -D_A \frac{\partial C_A}{\partial x} + C_A u_x$ yields, for constant u_x

$$\frac{\partial C_A}{\partial t} + u_x \frac{\partial C_A}{\partial x} = D_A \frac{\partial^2 C_A}{\partial x^2} - r_A \qquad (20)$$

Note that the left hand side of equation (20) is sometimes written as $\frac{DC_A}{Dt}$ and called "Stokes total time derivative." This is the rate of change of C_A an observer following the fluid (as in a drifting canoe) would notice. In contrast, $\frac{\partial C_A}{\partial t}$ denotes the rate of change an observer would note while standing at a fixed point in space (as on a bridge).

Extension to Three Dimensions

In three dimensions the balance is the same as in one dimension for the most part. The only additions are terms for flow in two other directions. The resulting equation is

$$\frac{\partial C_A}{\partial t} + u_x \frac{\partial C_A}{\partial x} + u_y \frac{\partial C_A}{\partial y} + u_z \frac{\partial C_A}{\partial z} = D_A \left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right] - r_A \qquad (21)$$

We can see the additional terms for convective flow in the y and z direction appear on the left hand side of the equation, and the additional terms for diffusional flow appear on the right hand side. As in the one dimensional case the left hand side of equation (21) corresponds to the time derivative "following the fluid." The velocity components in equation (21) are known for many simple flow situations, and, in principal, can always be found by solving the momentum balance (Navier-Stokes) equations. Equation (21) is the starting point for much current research in water technology. For example in this volume, Leeds will show how

the equation is used to simulate the behavior of streams and estuaries.[10]

NOTES

1. Species is used herein to denote a reactant or component of the system.
2. See, for example, R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, New York, John Wiley and Sons (1960), and R. C. L. Bosworth, "Transport Processes" in *Applied Chemistry*, New York, John Wiley and Sons (1956).
3. The expressions for the fluxes are actually much more complicated. However, for the conditions of main interest in water technology involving low concentrations of the diffusing species the expressions given here are assumed to be good approximations. These expressions are rigorously restricted to trace concentrations of the diffusing species in binary mixtures at constant total concentration, constant pressures, and constant temperature.
4. Swilley, E. L., J. O. Bryant and A. W. Busch, "Significance of Transport Phenomena in Biological Oxidation Processes," *Proceedings*, 19th Annual Industrial Waste Conference, Purdue University (1964).
5. Busch, A. W., L. T. Grady, Shivaji Rao, and E. L. Swilley, "Short-Term Total Oxygen Demand Test," *J. Water Pollution Control Federation*, XXXIV (1962), 354-362.
6. Ramkrishna, D., A. G. Fredrickson, and H. M. Tsuchiya, "Mathematical Models for the Dynamics of Microbial Growth-Structured Models Considering Inhibitors," *Industrial Engineering Chemical Research Results Manuscript*, MS-65-375-1 (1965).
7. Deans, H. A., "Kinetics on the Microbial Scale," This Volume.
8. Ibid.
9. Ramkrishna, Fredrickson and Tsuchiya, op. cit.
10. Leeds, J. V., Jr., "Mathematics of Stream and Estuary Problems," This Volume.

NOMENCLATURE

C_A	Concentration of "A," the diffusing species, moles per unit volume.
C_{Ai}	In the liquid phase away from the microbial phase.
C_{Ao}	In the microbial phase.
C_i	Initial concentration in the liquid phase.
D_A	Fickian diffusion coefficient for species "A," square units of length per unit time.
f	A ratio defined after equation (13).
g	Defined by equation (14).
k	The "true" first order reaction rate constant, see equation (4).
K	The "apparent" first order reaction rate constant, defined by equations (9) and (10).
m	The number of microbial particles.
N_{AX}	The flux of species "A" in moles per unit area per unit time in the x direction.
r	Radial position in spherical coordinates.
r_o	Radius of the (assumed spherical) microbe.
r_A	Rate of disappearance of "A" in chemical reaction moles per unit time per unit volume.
R	Total rate of disappearance of "A," moles per unit time.
S	Cross section area for flow.
t	Time.
x, y, z	Rectangular cartesian coordinates.
u	The fluid velocity vector, having components u_x, u_y, u_z in the respective directions.

V Total microbial volume in the system.
V_i Initial microbial volume in the system.
V_s Total liquid volume in the system.
W_A Weight fraction of species "A."
δ Thickness of the hypothetical stagnant "film."
α A stoichiometric coefficient defined by equation (9).
ρ Density.